

**ENVIRONMENTAL FORENSIC INVESTIGATION
OF SUBSURFACE PIPES CONTAINING TAR RESIDUES
NEAR A FORMER MGP IN ASHLAND, WI**

- FINAL REPORT -

Submitted to:

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1.0 OBJECTIVE

The purpose of this project was the detailed characterization of the hydrocarbons in non-aqueous phase liquid (NAPL), solid, and water samples collected from multiple subsurface pipes located between a former manufactured gas plant (MGP) site in Ashland, WI and selected down gradient locations proximate to the shoreline of Lake Superior. The data collected during this project provided the basis to determine whether the tar residue in the subsurface pipes was a source of elevated polycyclic aromatic hydrocarbons (PAH) measured in the selected down gradient locations. Battelle Memorial Institute (Battelle) conducted an environmental forensic investigation tailored for the analysis of MGP-derived tar and petroleum source signatures to satisfy these objectives. Its high-resolution chemical “fingerprinting” methods (GC/FID and GC/MS) focused on the aromatic and aliphatic composition of tar and petroleum thought to be present in the samples.

2.0 BACKGROUND

The Ashland MGP operated from the late 1800’s to the 1940’s as a manufactured gas plant using the carbureted water gas process. Coal, coke and/or petroleum feed stocks were presumably delivered to the facility via a nearby railroad line. A lumber mill that operated on the shore of Lake Superior was located topographically and hydrologically down gradient from the Ashland MGP site. This lumber facility generated a considerable quantity of wood scrap that, over the years, was distributed throughout the local coastline area. Approximately 100 feet of shoreline immediately down gradient from the Ashland MGP was filled since the MGP began operating.

Today, the subsurface soils, groundwater and sediments down gradient from the Ashland MGP are contaminated with PAH. Currently, it is not known if the PAH detected around the Lake Superior shoreline are from one or more sources. Past investigations at the site determined that the aliphatic and aromatic hydrocarbon composition of selected up and down gradient samples were significantly different, thereby suggesting the MGP operation was not the source of the PAH in the down gradient locations. However, this conclusion was not based on detailed (molecular level) “fingerprinting” data and was issued prior to the recent investigation of potential migration pathways leading from the former MGP toward Lake Superior.

This investigation revealed the presence of multiple subsurface pipes that potentially connected the former MGP with the former shoreline of Lake Superior. The buried steel and clay pipes were traced, uncovered, and sampled at different locations on three occasions. In July 2001, samples were collected from the down gradient section of the clay pipe and in the immediate vicinity of the discharge (seep) area. In addition, one monitoring well location above, and two monitoring well locations below the clay pipe were sampled (Figure 1). In September 2001, samples were collected from several up gradient sections of the buried clay pipe (Figure 1). Finally, in November 2001, samples were collected from two steel pipes of a different diameter that were located up gradient from the clay pipe and proximate to the former MGP site. Collectively, all of these samples were analyzed for the purpose of characterizing the hydrocarbon residues in and around the various pipes and comparing them to the water and solid samples collected down gradient from the pipes in the potential release areas.

3.0 METHODS

A summary of the methods for sample preservation and analysis at Battelle are presented in this section. Complete documentation of the chemical analysis described in this report, including a Quality Management Plan, a Quality Assurance Project Plan (QAPP), Standard Operating Procedures, chain-of-custody records, and raw and reduced data logs are archived at Battelle Memorial Institute in Duxbury, MA.

3.1 Sample Collection and Shipping

Representatives of Short Elliot Hendrickson, Inc. (SEH) and Wisconsin Department of Natural Resources (WDNR) collected and shipped sixteen samples in three shipments from July to November 2001. The matrices included NAPL, solid (soil and/or solidified organic material), and aqueous (water and/or sheens) residues. The samples were shipped by overnight courier in sample containers fitted with Teflon-lined caps. The three sample deliveries were received at Battelle at temperatures of $< 4^{\circ}\text{C}$, 1.3°C and ambient temperature, respectively. The samples were received and stored according to the Battelle chain-of-custody procedures. The field chain of custody and sample receipt information is provided in Attachment 10.

The field sample identifications, locations, collection dates, and matrices for the samples studied are summarized in Table 1a. The field sample ID's were abbreviated (see Table 1b) to simplify the tables and figures used for data presentation. Also, in tables and figures throughout this report the samples are listed in order from approximately the most up gradient locations (i.e., nearest to Ashland MGP) to the most down gradient locations (i.e., nearest to Lake Superior).

3.2 Chemical Analysis

The samples were prepared and analyzed in accordance with published methods (Stout et al., 2002) and as described in the QAPP. A summary of the analytical parameters is presented in Table 1b.

3.2.1 Sample Preparation

A mass of solid sample (5 to 10 g) was fortified with surrogates, dried with sodium sulfate and serially shake extracted with dichloromethane (DCM). Less sample mass (0.05 g to 2 g) was used for samples with a large quantity of organic material. Approximately one liter of water (sometimes containing sheens) was extracted by separatory funnel using DCM. The sample extracts were concentrated by Kuderna-Danish and nitrogen blow down techniques. The NAPL samples were diluted to approximately 10 mg/ml in DCM. The surrogates (naphthalene-d₈, phenanthrene-d₁₀, and chrysene-d₁₂) were quality control compounds added at the beginning of the method and used to document performance. The sample extracts and diluents were fortified with internal standards and split for GC/FID and GC/MS/SIM analyses (described below).

3.2.2 High Resolution Hydrocarbon Fingerprinting (GC/FID)

The sample extracts were analyzed using a high-resolution gas chromatograph equipped with a flame ionization detector (GC/FID). High-resolution hydrocarbon fingerprints were generated over a broad carbon range (C₉-C₄₀) that provided an overall assessment of the non-volatile hydrocarbons present in each sample, including the primary PAH analytes of concern. The GC/FID fingerprints for each field and QC sample are found in Attachment 3. These fingerprints provided information on the overall nature of the extractable hydrocarbons that were present, including the general PAH composition, variability, and degree of weathering.

3.2.3 Diagnostic PAH and SVOC (GC/MS/SIM)

The sample extracts were also analyzed using a high-resolution gas chromatograph equipped with a mass spectrometer operated in the selected ion monitoring mode (GC/MS/SIM). The instrument was calibrated to allow for quantification of a broad range of 2- through 6-ring PAH, selected alkylated PAH homologues, selected sulfur-containing compounds (benzothiophenes and dibenzothiophenes), and other compounds useful for the identification of hydrocarbon sources in the environment. An inventory of the target compounds is found in Table 2, along with abbreviations used in selected figures in this report. The concentration of target compounds in the field samples are presented in Attachment 4. Collectively, the concentration of these target compounds are useful for qualitatively and quantitatively relating samples from the suspected source and release areas.

3.2.4 Biomarker Fingerprints (GC/MS/SIM)

Environmental forensic investigators have demonstrated that the presence and/or pattern of biomarkers can reveal information about the specific source(s) of petrogenic residues in the environment; e.g., petroleum or coal (Stout *et al.*, 2002). For this project, selected biomarker fingerprints were qualitatively generated using GC/MS/SIM that monitored for diagnostic fragment ions. These analyses were conducted on the same sample extracts prepared for the measurement of PAH. While the GC/MS was not calibrated for the full suite of biomarkers, several quality control measures for tuning, linearity and mass discrimination ensured that the acquired biomarker patterns were suitable for a qualitative comparison among the samples.

4.0 RESULTS

The high-resolution hydrocarbon fingerprints, quantitative PAH data, PAH histograms, and biomarker fingerprints are presented in Attachments 3 through 9. In the following sections, the data are described with the project objective in mind, i.e., determination of chemical relationships among the field samples.

4.1 High-Resolution Hydrocarbon Fingerprints

Resolved peaks representing the parent (non-alkylated) PAH, ranging from naphthalene to benzo(g,h,i)perylene, constituted the dominant feature of the high-resolution hydrocarbon fingerprints (Attachment 3). The distribution and predominance of parent PAH in each of the field samples was entirely consistent with those derived from MGP tar. (See the fingerprint for a coal tar reference material, ZL44CT, near the end of Attachment 3, for comparison). The hydrocarbon fingerprints reveal no obvious evidence for the presence of any other source of hydrocarbons in the samples studied.

The fingerprints do reveal that the primary variation among the field samples was in the degree of environmental weathering. The degree of weathering was most easily recognized by comparing the number and height of resolved peaks eluting before Androstane¹ (i.e., light or lower molecular weight PAH) relative to those eluting after Androstane (heavy or higher molecular weight PAH) (Figure 2). As expected given the greater susceptibility of lower molecular weight PAH to environmental weathering, those samples exhibiting a more highly weathered tar fingerprint were relatively depleted in lower molecular weight PAH and *vice versa* (Figure 2).

Although the samples did vary in the degree of weathering (Figure 2), overall they were only slightly-to-moderately weathered, as evidenced by the presence of light, lower molecular weight compounds in even the most highly weathered field samples (e.g. MW-7 in Figure 2d). Even though sample MW-7 exhibited

¹ The peaks labeled OTP (surrogate) and Androstane (internal standard) are quality control compounds that should otherwise be visually ignored for the interpretation of the hydrocarbon fingerprints.

the largest relative losses in the light, low molecular weight PAH among all of the field samples, it still retained a significant abundance of light PAH. This light to moderate weathering improved the likelihood that source signatures in the light PAH range may not have been compromised by environmental weathering.

The water sample from the East Riser location exhibited a particularly high predominance of low molecular weight PAH and very little heavy, high molecular weight PAH (Figure 2b). This fingerprint cannot be reasonably attributed to a “lack of weathering” of an MGP tar. Instead, it is likely that the elevated concentrations of light PAH in the water sample indicate the presence of MGP drip oil² or the water-soluble fraction of MGP tar. Given the low concentration of total PAH in the East Riser sample (Table 3), it is more likely that the East Riser sample represents a water-soluble fraction of MGP tar (rather than drip oil), which suggests that the dissolution of PAH from MGP tar was an active process within the pipeline system.

4.2 PAH Histograms

The PAH concentration data (Attachment 4) can be used to construct PAH histograms that help visualize the PAH data for comparative purposes. PAH histograms for the samples studied appear in Attachment 6; PAH abbreviations used in the histograms were shown in Table 2. Specifically, the histograms quantitatively illustrate the overall relationship between the low and high molecular weight PAH, as well as the specific distribution of PAH homologues with varying levels of alkylation (Figure 3). While the hydrocarbon fingerprints (described above) qualitatively depict all of the extractable hydrocarbons in the analytical range, the PAH concentration data/histograms offer greater detail and more quantitative measurements of the target hydrocarbons (Attachment 4).

Some terminology should be briefly discussed before the PAH histograms are described. The term “parent” or “non-alkylated” PAH refers to a polycyclic aromatic hydrocarbon that possesses no hydrocarbon side chains. By contrast, “alkylated” or “alkyl” PAH refers to a polycyclic aromatic hydrocarbon that possesses one or more saturated hydrocarbon side chains. For the data shown in Attachment 4 (and compounds listed in Table 2), the number of carbons in the side chain(s) is indicated in the abbreviated analyte prefix; for example, polycyclic aromatic hydrocarbon analytes with one, two, three, or four member carbon side chains received the “C1-“, “C2-“, “C3-“, and “C4-“ prefixes, respectively.

The concentration axis of the histograms was adjusted to the maximum target analyte for each sample to improve visual comparability. The analyte list and abbreviations used for the histograms are presented in Table 2. The histograms of relevant reference materials from Battelle’s comprehensive database/library are presented in Attachment 5 in order to illustrate the difference between selected petrogenic and pyrogenic signatures.³ (See Figure A5-1 found in Attachment 5).

A review of the PAH histograms clearly reveals a pyrogenic pattern consistent with MGP tar was detected in all field samples. This was evidenced by the higher abundance of parent PAH relative to alkylated PAH, which gives each homologous series of the (unweathered) analytes a ‘sloped’ appearance (Stout et al., 2002). Additional reference material histograms illustrate the existence of differences among the pyrogenic PAH patterns of carbureted water gas and coal tars (See Figure A5-2 in Attachment 5). The relative abundance of fluoranthene and pyrene was very similar among the field samples (e.g., Figure 3) and was most consistent with carbureted water gas tar presented in Figure A5-2.

² Drip oil is an MGP condensate typically recovered throughout the gas distribution system of the plant.

³ The term, “petrogenic,” refers to the formation of PAH during petroleum or coal generation (Stout et al., 2002). By contrast, the term, “pyrogenic,” refers to the formation of PAH during the partial combustion or pyrolysis of organic matter (Stout et al., 2002).

Inspection of the PAH histograms illustrates a high degree of similarity among the samples collected from the pipes and those collected from the release areas (e.g., Figure 3). With one exception, all of the samples exhibited very similar patterns among the highest molecular weight (i.e. most recalcitrant) PAH. The recalcitrant, highest molecular weight PAH were functionally defined as 5- and 6-ring PAH (benzofluoranthenes through benzo(g,h,i)perylene; Table 2). The relative distributions among these PAH reflect the specific conditions of their formation; for example, the carburetion procedure/conditions and feedstock. The East Riser water sample deviated from the common pattern of heavy PAH and exhibited a PAH profile (and hydrocarbon fingerprint) that was consistent with the water-soluble fraction of MGP tar.

Some subtle differences among the samples were observed in the 4-ring PAH group (fluoranthene through chrysene in Table 2). Specifically, the samples from the steel pipe exhibited slightly lower relative abundances of parent to alkylated PAH within the 4-ring group. This difference was significant given the absence of severe PAH weathering (see hydrocarbon fingerprint discussion above); consequently, weathering of these stable analytes was unlikely. Instead this difference tends to indicate the presence of a slightly different type of tar in the steel pipe sampling locations (as compared to tar in the clay pipe locations). This slightly different type of tar in the steel pipe areas would appear to have been formed from a different or modified carburetion process and/or feedstock.

Obvious differences were observed in the PAH histograms among the 2- to 3-ring PAH (Figure 3). As expected, these differences were consistent with range of environmental weathering evident in the hydrocarbon fingerprints. While MGP tars formed differently can exhibit some source specific PAH distributions in this range (e.g., Figure A5-2 in Attachment 5), the potential effects of weathering in this molecular weight range complicates any interpretation. Nevertheless, close inspection of the PAH histograms reveals that the steel pipe samples contained a slightly higher abundance of dibenzofuran relative to fluorene than the samples from the clay pipe and down gradient release area. However, the samples from the clay pipe and the potential release area (MW-7 and TW-9) were very similar.

4.3 Principal Components Analysis of PAH Data

Principal components analysis (PCA) is a numerical analysis tool that is commonly used to explore the complex chemical differences or similarities among many samples. In this study, PCA was used as an exploratory tool to visualize the inter-sample and inter-variable relationships among the PAH dataset. It was performed by using the Ein*Sight software product (Version 4.0; Infometrix, Inc., Seattle, WA). PCA output includes a distribution of samples (e.g., pipe and release area samples) in n-dimensional space, where n was the number of input variables (e.g., PAH analytes or ratios). The Euclidean distance between sample points on the resulting factor score plots represented the variance captured in each principle component (PC). In simple terms, samples that cluster together are considered chemically similar and outliers are considered chemically distinct. A factor loading is simultaneously calculated for each variable (e.g., PAH analyte) contributing to each PC. A cross plot of the factor loadings for the corresponding PCs revealed the individual variables (PAH analytes or ratios) that were responsible for the variance in each PC. The PAH analyte concentrations or ratios were normalized prior to PCA in order to minimize the influence of concentration. Thus, the PCA focused on distinguishing the similarities and differences in PAH patterns irrespective of analyte concentration.

The chemical signatures of different pyrogenic materials (e.g. MGP tars) can be illustrated by comparing the relative content among functional groups that are preferentially pyrolyzed or condensed during industrial carburetion (Emsbo-Mattingly *et al.*, 2001). Useful parameters include the relative abundance of (1) PAH with variously alkylated hydrocarbon side-chains (e.g., parent PAH *versus* C2- and C3 alkylated PAH), (2) sulfur-containing PAH (e.g., dibenzothiophenes), and (3) 5-ring PAH with different ring structures. In general, ratios that capture the relative abundance of these functional groups, as well as

selected ratios among various 6-ring PAH of similar molecular weight, can be used to distinguish between different types of MGP wastes in the environment (Emsbo-Mattingly et al., 2001). Thus, selected and diagnostic ratios were calculated for each of the field samples. These ratios were used as input variables for PCA, allowing for the detailed comparison among the samples (Table 4).

The factor score plot of the first and second principal components is shown in Figure 4a. The corresponding factor loadings plot is shown in Figure 4b. Recall, samples that plot near to one another in the factor score plot are chemically similar, whereas those that plot apart are chemically distinct. The clustering of samples in the upper left hand quadrant of the factor score plot includes samples from the clay pipe and from the down gradient release area (Figure 4a). This clustering indicates that the MGP tar in the clay pipe samples was chemically comparable to the samples from the down gradient release area. For example, many of the samples collected from the clay pipe grouped closely with the down gradient sample TW-9 (Figure 4a). Thus, the clay pipe appears to be a likely source of PAH in samples collected from the down gradient release area.

PCA determined that the East Riser sample was unique among those studied (Figure 4a). Recall, this was the sample believed to contain the water-soluble fraction of MGP tar (see above). As might be expected, the factor loadings plot (Figure 4b) reveals the East Riser sample was enriched in parent PAH (relative to alkylated PAH), with a particular enrichment of light, low molecular weight parent PAH (i.e., naphthalene, phenanthrene, and anthracene). As revealed by the hydrocarbon fingerprint and PAH histogram, the PCA results reflect the unique presence of the water-soluble fraction of MGP tar in this sample.

PCA also revealed that the two samples (one a duplicate) of solidified tar collected around the clay pipe discharge were slightly depleted in light, low molecular weight PAH (Figure 4). These samples are slightly offset from the other clay pipe and discharge (water) samples. Environmental weathering has likely caused this depletion of light PAH in the solid discharge samples. The reduction of light PAH, combined with the elevated relative abundance of sulfur-containing PAH (dibenzothiophenes), distinguished MW-7 from the clay pipe samples (Figure 4). The reduction in light PAH in this sample was also attributed to weathering. Recall, the MW-7 sample was the most weathered sample studied (Figure 3). The relative enrichment of dibenzothiophenes in the MW-7 sample may also be due to weathering, or may indicate the trace presence of a localized release of uncombusted fuel and gas oil.

Finally, PCA revealed that the two steel pipe samples were comparable to one another, but exhibited slightly different distributions of diagnostic source ratios than those from the clay pipe (Figure 4a). This suggests that the MGP tar in the steel pipe area is distinct from the MGP tar from the clay pipe. Figure 4b shows that the MGP tar from the steel pipes were differentiated in part by the elevated ratio of dibenzofuran to fluorene and acenaphthylene to acenaphthene and a higher relative abundance of alkylated PAH.

4.4 Biomarker Fingerprints

Four categories of biomarker fingerprints were used to determine the type of petrogenic residues present in the samples. The categories included normal alkanes (as determined by m/z 85 mass chromatograms), alkylcyclohexanes (m/z 83), terpanes (m/z 191), and steranes (m/z 217). These fingerprints provided detailed chemical information that spans a wide molecular weight range. They can be found in Attachments 7 through 9. These fingerprints are useful in the detection and characterization of different petroleum (and perhaps coal) sources, as were used during the operational history of former MGPs. The normal alkanes and alkylcyclohexanes span almost the entire hydrocarbon range from nC_9 to nC_{36} . By contrast, the terpanes and steranes are generally found in crude oil and in heavier fuel and lubricating oils.

However, a great deal of information is available on the relationship of these recalcitrant analytes to the processes that generated the petroleum

The normal alkane and alkylcyclohexane fingerprints for the samples studied revealed four basic patterns (Figure 5; Attachment 7). First, the two samples from the steel pipe exhibited a relatively narrow range of normal alkanes in the nonane (nC9) to nonadecane (nC19) range (Figure 5a). Second, the East Riser sample featured trace, if any, normal alkanes amidst the high concentrations of light PAH (Figure 5b). However, trace levels were detected between nC22 and nC33. Third, the bulk of the clay pipe samples contained a wide range, middle distillate petroleum product(s) signature ranging from nC9 to nC27 with a maximum around nC12 to nC13 (e.g. Figure 5c). Fourth, the Solids Around the Discharge Pipe, MW-7, and TW-9 exhibited the same wide range petroleum product(s) signature that the clay pipe samples did, but this appears to be superimposed on another signature exhibiting elevated levels of isoprenoid hydrocarbons (e.g., Figure 5d). This pattern is consistent with a mixture of a relatively weathered petroleum product(s) enriched in the more recalcitrant isoprenoids and an unweathered (or less weathered) petroleum product(s) that is relatively enriched in normal alkanes.

It is notable that close inspection of the m/z 85 mass chromatograms (Attachment 7) reveals that the abundance of heptadecane relative to pristane (nC17/Pr) declined from its highest level at TW-13 (up gradient) to its lowest level in MW-7 (down gradient), while exhibiting intermediate though varying levels throughout the length of the clay pipe. The relative reduction of heptadecane with increasing distance down gradient would be consistent with increasing levels of biodegradation in at least some petroleum components and/or relative abundance of the more highly weathered petroleum component recognized in MW-7.

Inspection of the m/z 191 mass chromatograms (Attachment 8) revealed four terpane fingerprints patterns that are represented in Figure 6. First, the two steel pipe samples contained no terpanes above the analytical detection limit (Figure 6a). This finding is consistent with the previous observation that these samples contained a lighter and narrower range (nC9-nC19) petroleum product that would not be expected to contain these terpane biomarkers. Second, the majority of samples collected from the clay pipe and down gradient locations contained a full suite of terpane biomarkers (e.g., Figure 6b). Their presence (along with the n-alkane patterns described above) indicates the likely presence of a heavier fuel or gas oil in the clay pipe and down gradient samples. Third, the Pipe Sludge Center of Yard and Scrapings from Inside Discharge contained the pentacyclic triterpane, oleanane, which suggested that the petroleum in these samples originated from a separate source from, or contains a petroleum component that is distinct from, those observed in the clay pipe and discharge area. Fourth, the higher abundance of the biomarker Ts relative to Tm in sample MW-7 was considered characteristic of an independent source of petroleum. This interpretation was consistent with the localized elevation of dibenzothiophenes measured in MW-7 and supported the assertion that a second type of petroleum may have impacted this sampling location.

The low levels of steranes prevented a thorough interpretation.

5.0 CONCLUSIONS

Advanced chemical analyses were performed on each site sample. The results of these analyses generated the following conclusions:

- The high-resolution fingerprints indicated the presence of MGP tar in all the field samples.
- The distribution of PAH in all field samples was most consistent with a carbureted water gas tar.

- With the exception of the East Riser sample, the PAH histograms indicated that the samples were all very similar to one another regardless of their collection location.
- The East Riser sample was unique and appeared to be the water-soluble fraction of MGP tar. This pattern suggested that the aqueous dissolution of tar was an active weathering process within the pipeline system. Supporting this contention was the fact that the trace pattern of heavy, high molecular weight PAH in the East Riser sample matched other samples from the clay pipe system.
- Although the patterns of PAH were similar among the field samples, a detailed inspection of the PAH histograms and principal components analysis helped to differentiate the two, up gradient steel pipe samples from remaining down gradient field samples. This difference suggested that the MGP tar in the steel pipe area was distinct from that in the clay pipe system. The difference likely indicated that the tar in the steel pipe was produced under slightly different operating conditions and/or from a different feedstock.
- Differences in the MGP tar residues among the samples collected from the clay pipe and down gradient locations were attributed to environmental weathering. The heavy molecular weight portion of the tar in the clay pipe and down gradient samples, i.e., that portion least affected by weathering, was nearly identical and indicated a common source.
- While the more highly weathered PAH pattern of MW-7 still resembled the pattern in the clay pipe samples, the slightly higher relative abundance of sulfur-containing PAH and a diagnostic terpane biomarker pattern revealed the possible coexistence of uncombusted fuel or gas oil at this location.
- The petrogenic residues in the field samples were more variable than the MGP tar residues. The petrogenic residues could be qualitatively differentiated into five potential sources. Distinct petroleum patterns were detected in the steel pipe samples (relatively light weight), East Riser sample (trace level biomarkers similar to heavy weight range of the fuel oil measured in the other clay pipe samples), remaining clay pipe samples listed in Table 1 (wide range fuel or gas oil), MW-7 sample (similar to clay pipe samples with elevated an level of Ts relative to Tm), down gradient samples including Solids Around Discharge Pipe, MW-7, and TW-9 (elevated isoprenoid hydrocarbons overprinted on clay pipe pattern suggestive of mixed unweathered and weathered petroleum products).
- The varying abundance of heptadecane relative to pristane among the clay pipe and down gradient samples indicated that the weathering state of the petroleum in the clay pipe system may have been influenced by biodegradation, generally increasing in a down gradient direction.

The pyrogenic (PAH) and petrogenic (biomarkers) patterns independently identified two types of MGP tars in the field samples. The first type of tar was located in the steel pipes and the second type was located in both the clay pipe system and in the down gradient sampling stations. The petrogenic (biomarker) patterns also indicated the presence of residual petroleum refined from different crude oils. The weathering patterns observed included the dissolution of PAH (i.e., formation of a water-soluble fraction) and the biodegradation of petroleum. This finding did not exclude the possible existence of other weathering processes.

6.0 SUMMARY

Based on the conclusions stated in Section 5.0, this section proposes a conceptual site model that could account for the analyte distributions recorded in this report.

- During the operation of the former MGP, tar was transported via the subsurface pipes that were sampled during July, September, and November of 2001. The tar signatures detected in these pipes were consistent with one another and with the chemical signature of carbureted water gas

tars reported in the literature; for example, the ratio of fluoranthene to pyrene was less than 1.0 (Emsbo-Mattingly *et al.*, 2001; EPRI, 1993).

- The clay pipe(s) likely permitted the release of waste tar from an up gradient location near the former MGP in Ashland WI to approximately the former shoreline of Lake Superior. The samples collected down gradient of the pipes were chemically similar to the clay pipe samples. Consequently, the clay pipe samples and down gradient samples contain MGP tar(s) that likely originated from a similar carburetion process. The outer perimeter of this clay pipe signature extended minimally to the TW-9 sample collection station. Once the waste tar was discharged from the clay pipe, it may have migrated or been transported to proximate locations, like TW-9, around the former shoreline of Lake Superior as dictated by the developmental history of the shoreline area.
- Some variability existed in the relative abundance of the light constituents of these tars due to multiple weathering processes; for example, the East Riser sample, which was comprised of the water-soluble fraction of MGP tar, demonstrated that the dissolution of PAH from the tar had occurred and/or the declining abundance of heptadecane relative to pristane indicated the biodegradation of petroleum residue had occurred.
- Sample MW-7 differed chemically from the pipe samples in terms of its higher relative content sulfur-containing and alkylated PAH. A localized release of petroleum in the vicinity of MW-7 may have enriched these analytes. This sampling location may have been influenced by releases associated with gas oil supply transfers from the railroad.
- The tar samples collected in November 2001 from the 2" and 12" steel pipes were chemically distinct from samples collected from other locations and may reflect an alternate carburetion feed stock, modified MGP operating condition, or equipment upgrades that occurred commonly during the history of former MGPs (Emsbo-Mattingly *et al.*, 2001).
- The biomarker patterns varied occasionally within the clay pipe samples and among samples with similar PAH patterns. This finding suggested that the MGP used multiple sources of gas oil in the carburetor unit.

7.0 REFERENCES

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Attachment 1

Figures

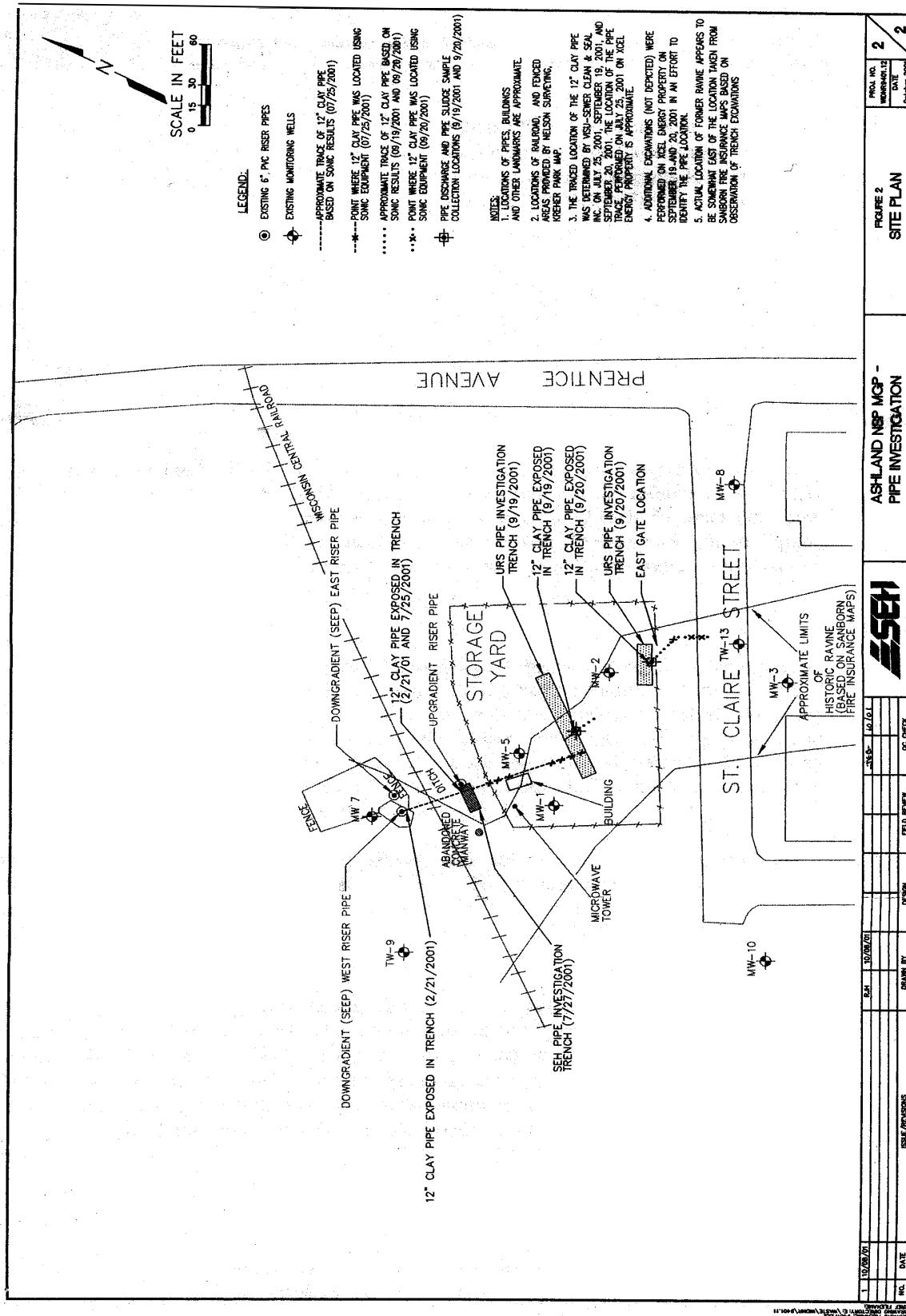
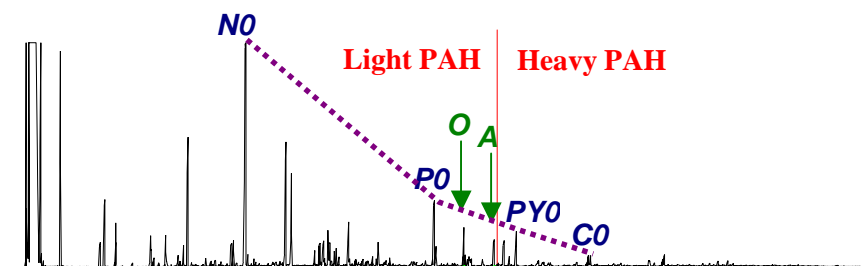
Figure 1.
Site Map

Figure 2.
High Resolution Fingerprints Illustrate Weathering Patterns

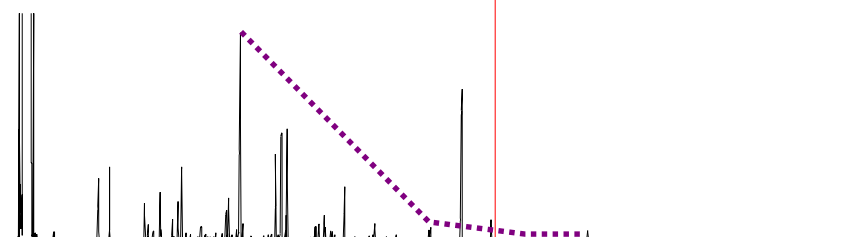
2a TW-13

Among Least Weathered
 of Field Samples
 Light > Heavy PAH



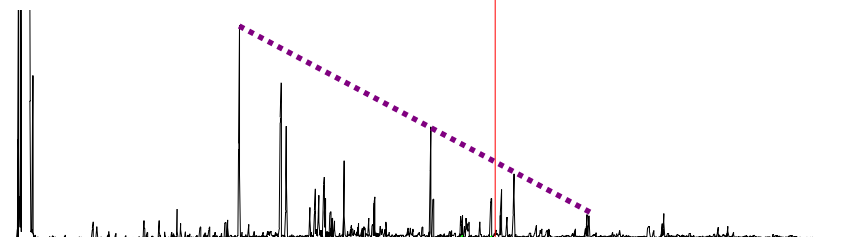
2b. East Riser

Water-soluble Fraction/
 Drip Oil
 Light >> Heavy PAH



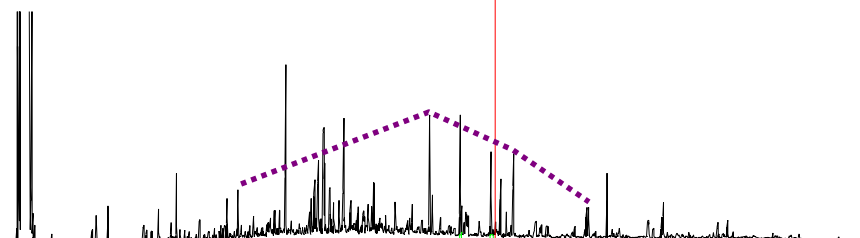
2c. Pipe Discharge

Light Weathering
 Light > Heavy PAH
 Like TW-13 with slightly
 less naphthalene
 relative to phenanthrene



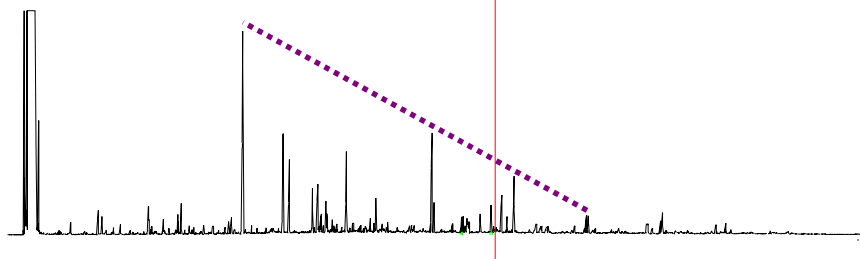
2d. MW-7

Most weathered
 of Field Samples
 Light > Heavy PAH
 Naphthalene < Phenanthrene



2e. TW-9

Like Pipe Discharge



N0 – Naphthalene P0 – Phenanthrene PY0 – Pyrene C0 – Chrysene
 A – Androstane (Internal Standard) O – ortho-Terphenyl (OTP) (Surrogate)

Figure 3.
PAH Histograms Illustrate Source and Weathering Patterns

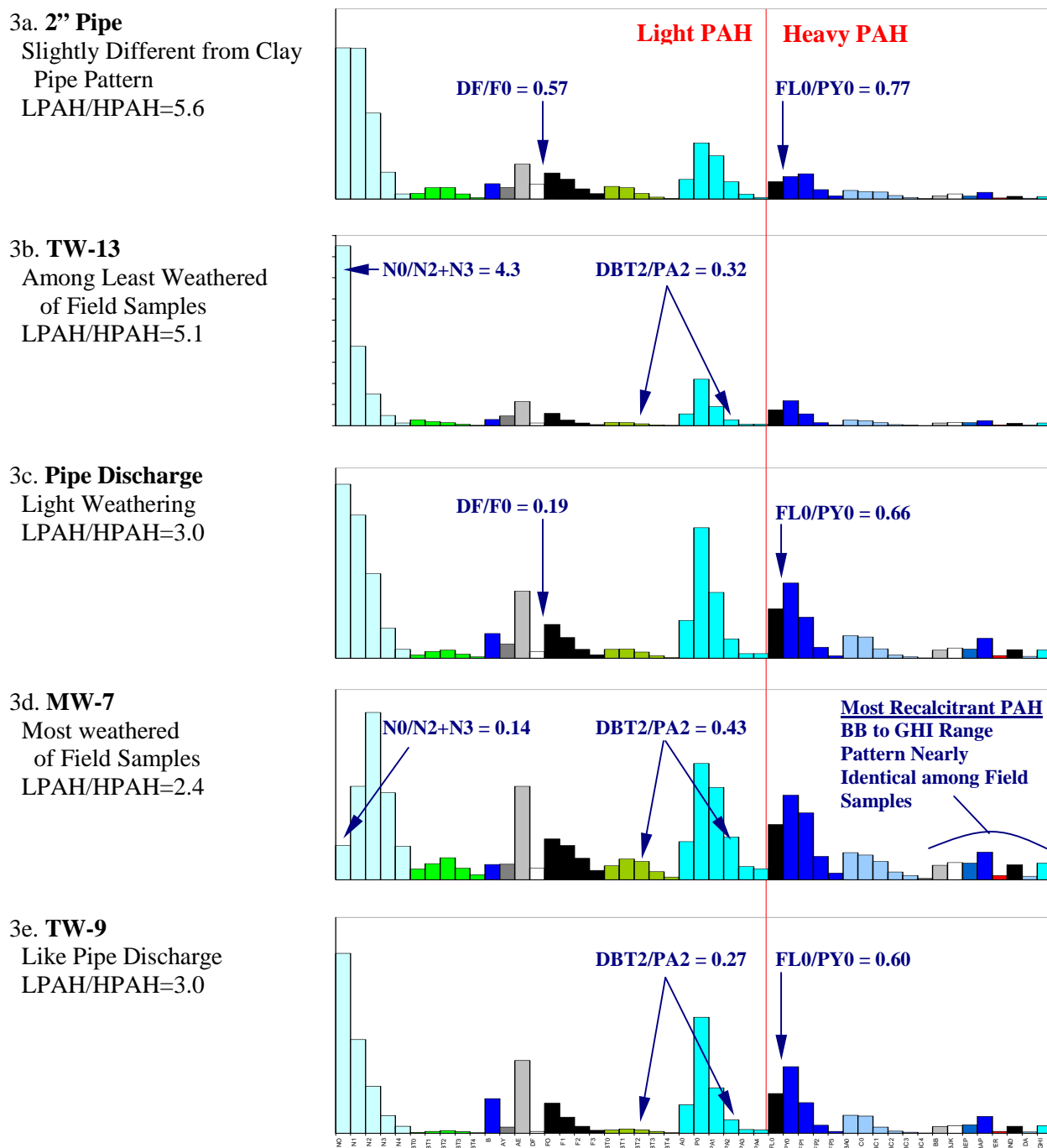
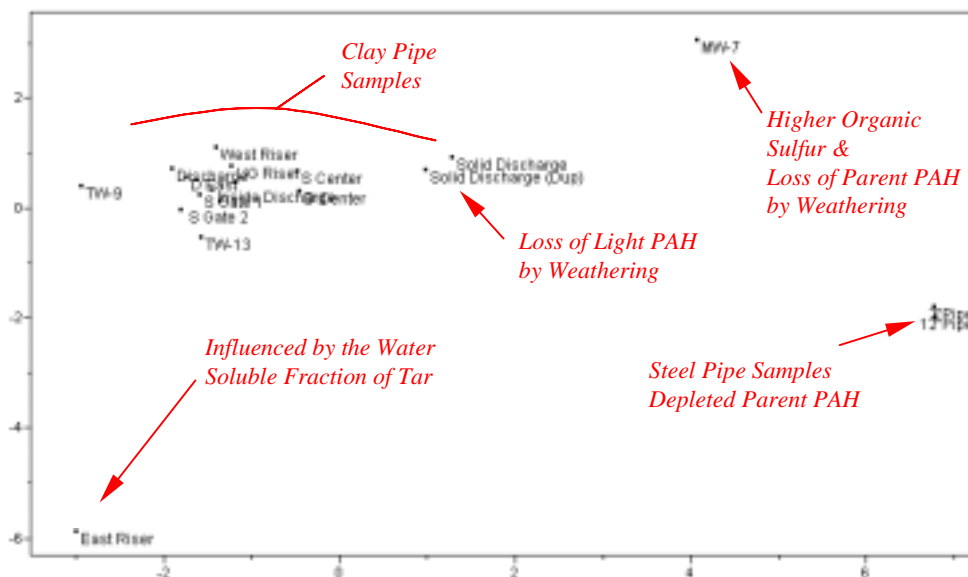


Figure 4. Principal Components Analysis (PCA) Using Selected Source Ratios

4a. Sample Groupings (PCA Scores Plot). Principal components 1 (x-axis) and 2 (y-axis) contain 62% and 23% of the variability, respectively.



4b. Analyte Groupings (PCA Loadings Plot).

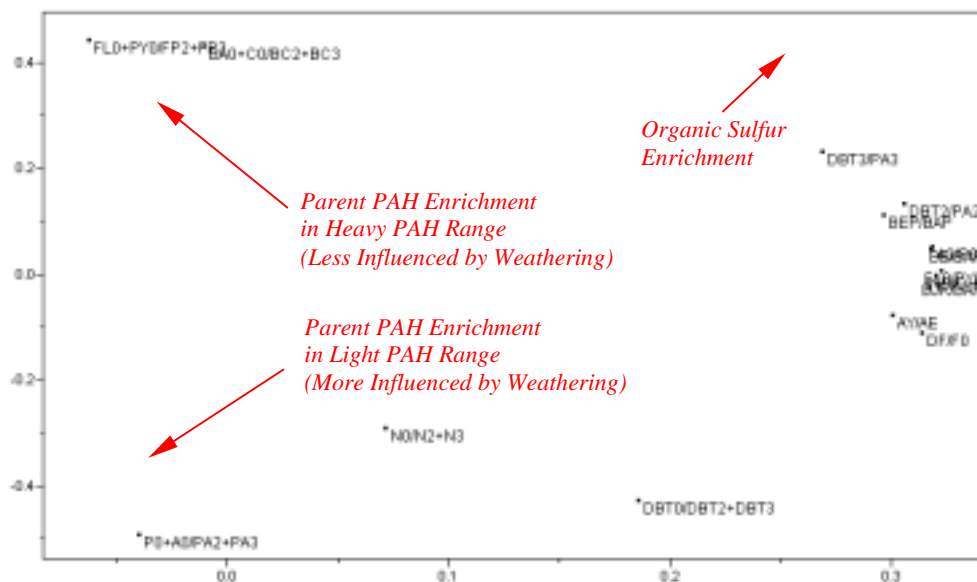
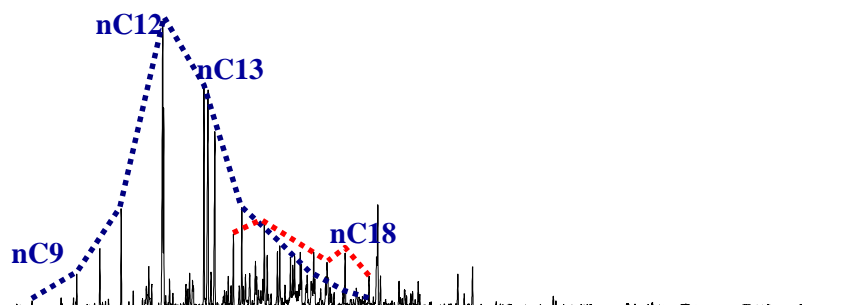


Figure 5.
Normal Alkane Biomarker Fingerprints
Reveal Multiple Types of Petroleum

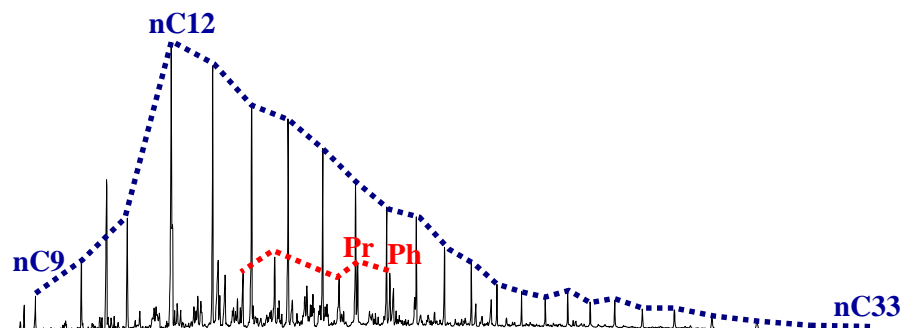
5a. 2" Pipe

Lighter Weight,
 Narrow Range Gas Oil
 Weathering state unknown



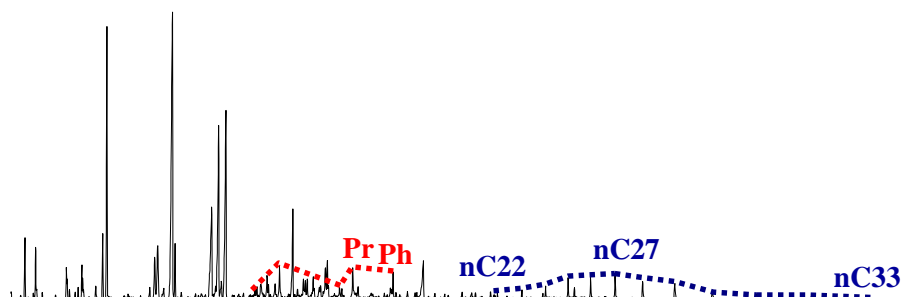
5b. TW-13

Wide Range Gas Oil
 Relatively unweathered



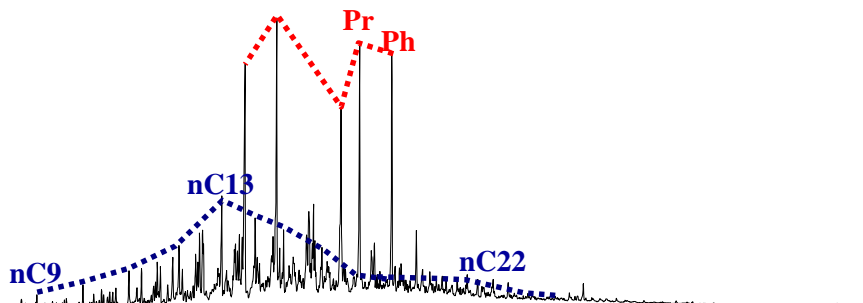
5c. East Riser

Water Soluble Fraction
 of MGP tar
 Light fraction of gas oil
 (nC9 to nC21) weathered
 Heavy fraction of gas oil
 present



5d. MW-7

Mixture of Unweathered
 Gas Oil (nC9 to nC22)
 and Weathered
 Middle to Heavy Weight
 Petroleum Product
 (elevated isoprenoids)



nC# = normal alkane containing # carbons in the chain
 (Blue Dash) peak to peak profile of the normal alkanes

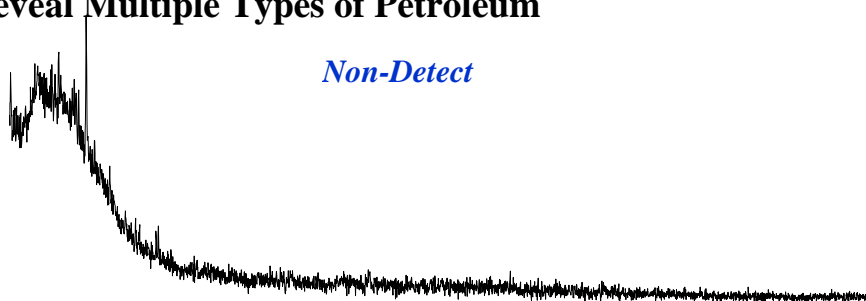
Pr = Pristane (isoprenoid hydrocarbon) Ph = Phytane (isoprenoid hydrocarbon)
 (Red Dash) peak to peak profile of selected isoprenoid hydrocarbons

Figure 6.
Terpane Biomarker Fingerprints
Reveal Multiple Types of Petroleum

6a. 2" Pipe

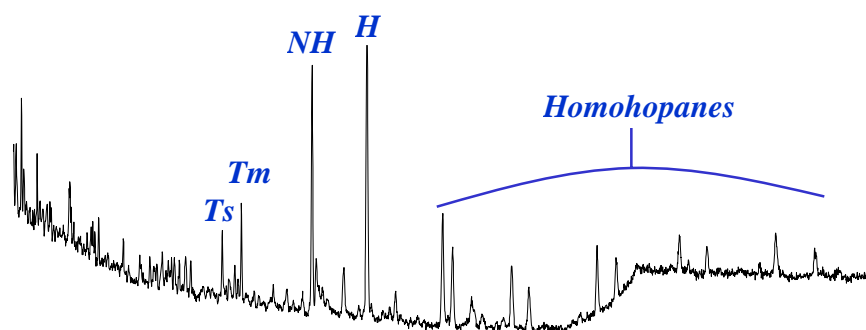
Lighter Weight,
 Narrow Range Gas Oil
 No Terpanes in Distillate

Non-Detect



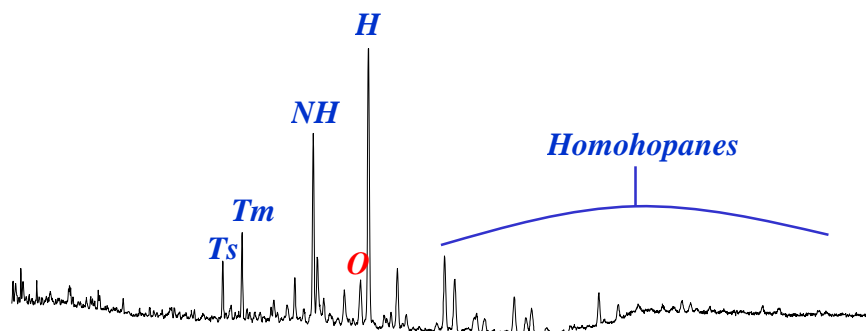
6b. TW-13

Wide Range Gas Oil
 Relatively unweathered
 Common pattern among
 field samples



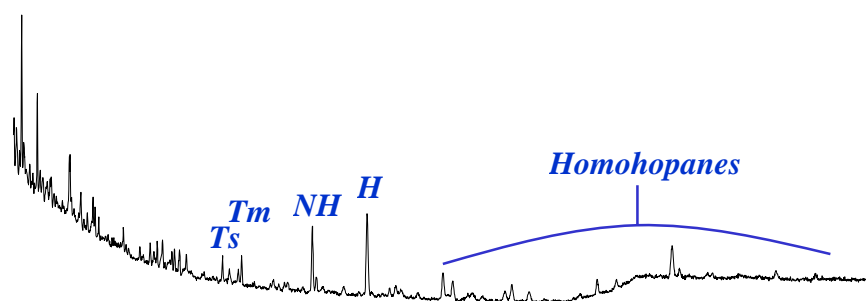
6c. East Riser

Water Soluble Fraction
 of MGP tar
 Biomarkers in heavy fraction
 of gas oil
 Presence of oleanane
 indicates an additional
 petroleum source



6d. MW-7

Mixture of Unweathered
 Gas Oil and Weathered
 Middle to Heavy Weight
 Petroleum Product
 Higher relative abundance of
 Ts suggests multiple
 petroleum sources



Ts = 18 α (H),21 β (H)-22,29,30-trisnorhopane Tm = 17 α (H),21 β (H)-22,29,30-trisnorhopane
 NH = 17 α (H),21 β (H)-30-norhopane H = 17 α (H),21 β (H)-hopane O = 18 α (H) & 18 β (H)-oleanane

Attachment 2

Tables

Table 1.
Sample Identification, Collection and Analysis Summary

1a. Sample Collection Summary.

Field Sample ID	Location (Listed ~ Up to Down Gradient)	Collection Date	Matrix
2 Inch Steel Pipe	Steel Pipe Near Former MGP	11/12/01	Oil (NAPL)
12 Inch Steel Pipe	Steel Pipe Near Former MGP	11/12/01	Oil (NAPL)
TW-13	Between MGP and Clay Pipe	7/24/01	Water
Pipe Discharge East Yard Gate	Up Gradient Clay Pipe	9/20/01	Solid
Pipe Sludge East Yard Gate #1	Clay Pipe	9/20/01	Solid
Pipe Sludge East Yard Gate #2	Clay Pipe	9/20/01	Solid
Pipe Discharge Center Of Yard	Clay Pipe	9/19/01	Solid
Pipe Sludge Center of Yard	Clay Pipe	9/19/01	Solid
Upgradient Riser	Clay Pipe	7/24/01	Water
East Riser	Clay Pipe	7/24/01	Water
West Riser	Clay Pipe	7/24/01	Water
Scrapings From Inside Discharge	Clay Pipe	7/25/01	Solid
Pipe Discharge	Down Gradient Terminus of Clay Pipe	7/25/01	Water
Solids Around Discharge Pipe	Proximate Release Area	7/25/01	Solid
MW-7	Intermediate Release Area	7/24/01	Water
TW-9	Most Distant Release Area	7/24/01	Water

1b. Sample Identification and Analysis Summary.

Field Sample ID	Hydrocarbon Fingerprint	Quantitative PAH	Biomarker Fingerprint	Battelle ID	Abbreviation
2 Inch Steel Pipe	X	X	X	W9071	2" Pipe
12 Inch Steel Pipe	X	X	X	W9072	12" Pipe
TW-13	X	X	X	W5548	TW-13
Pipe Discharge East Yard Gate	X	X	X	W6841	D East
Pipe Sludge East Yard Gate #1	X	X	X	W6839	S Gate 1
Pipe Sludge East Yard Gate #2	X	X	X	W6840	S Gate 2
Pipe Discharge Center Of Yard	X	X	X	W6837	D Center
Pipe Sludge Center of Yard	X	X	X	W6838	S Center
Upgradient Riser	X	X	X	W5547	UG Riser
East Riser	X	X	X	W5544	East Riser
West Riser	X	X	X	W5543	West Riser
Scrapings From Inside Discharge	X	X	X	W5551	Inside Discharge
Pipe Discharge	X	X	X	W5549	Discharge
Solids Around Discharge Pipe	X	X	X	W5550	Solid Discharge
MW-7	X	X	X	W5545	MW-7
TW-9	X	X	X	W5546	TW-9

Table 2.
Primary PAH Analytes and Abbreviations

Target Analyte	Abbreviation	
	Individual (Large Histogram)	Group (Small Histogram)
Naphthalene	NO	N
C1-Naphthalenes	N1	
C2-Naphthalenes	N2	
C3-Naphthalenes	N3	
C4-Naphthalenes	N4	
Benzo(b)thiophene	BT0	BT
C1-Benzo(b)thiophenes	BT1	
C2-Benzo(b)thiophenes	BT2	
C3-Benzo(b)thiophenes	BT3	
C4-Benzo(b)thiophenes	BT4	
Biphenyl	B	B
Acenaphthylene	AY	Y
Acenaphthene	AE	E
Dibenzofuran	DF	D
Fluorene	FO	F
C1-Fluorenes	F1	
C2-Fluorenes	F2	
C3-Fluorenes	F3	
Dibenzothiophene	DBT0	DBT
C1-Dibenzothiophenes	DBT1	
C2-Dibenzothiophenes	DBT2	
C3-Dibenzothiophenes	DBT3	
C4-Dibenzothiophenes	DBT4	
Anthracene	A0	PA
Phenanthrene	P0	
C1-Phenanthrenes/Anthracenes	PA1	
C2-Phenanthrenes/Anthracenes	PA2	
C3-Phenanthrenes/Anthracenes	PA3	
C4-Phenanthrenes/Anthracenes	PA4	
Fluoranthene	FL0	FP
Pyrene	PY0	
C1-Fluoranthenes/Pyrenes	FP1	
C2-Fluoranthenes/Pyrenes	FP2	
C3-Fluoranthenes/Pyrenes	FP3	
Benz[a]anthracene	BA0	BC
Chrysene	C0	
C1-Chrysenes	BC1	
C2-Chrysenes	BC2	
C3-Chrysenes	BC3	
Benzo[b]fluoranthene	BB	B
Benzo[j/k]fluoranthene	BJK	K
Benzo[a]fluoranthene	BAF	A
Benzo[e]pyrene	BEP	E
Benzo[a]pyrene	BAP	A
Perylene	PER	P
Indeno[1,2,3-c,d]pyrene	IND	I
Dibenz[a,h]anthracene	DA	D
Benzo[g,h,i]perylene	GHI	B

Table 3.
Total PAH Concentrations (ppm)

Client Sample ID	Matrix	TPAH ¹	Units	Rank ²	LPAH/HPAH
					Ratio ³
2 Inch Steel Pipe	Oil	136000	mg/Kg	1	5.6
12 Inch Steel Pipe	Oil	97800	mg/Kg	2	5.0
TW-13	Aqueous	13.1	mg/L	14	5.1
Pipe Discharge East Yard Gate	Solid	76000	mg/Kg	3	3.2
Pipe Sludge East Yard Gate #1	Solid	16200	mg/Kg	6	3.5
Pipe Sludge East Yard Gate #2	Solid	24000	mg/Kg	5	4.1
Pipe Discharge Center Of Yard	Solid	496	mg/Kg	11	3.0
Pipe Sludge Center of Yard	Solid	919	mg/Kg	10	2.3
Upgradient Riser	Aqueous	39.1	mg/L	13	2.8
East Riser	Aqueous	0.576	mg/L	16	46
West Riser	Aqueous	172	mg/L	12	2.4
Scrapings From Inside Discharge	Solid	29400	mg/Kg	4	3.3
Pipe Discharge	Aqueous	2880	mg/L	8	3.0
Solids Around Discharge Pipe	Solid	1500	mg/Kg	9	2.6
MW-7	Aqueous	2.71	mg/L	15	2.4
TW-9	Aqueous	5520	mg/L	7	3.0

1 - Total PAH (TPAH) is the sum of PAH from naphthalene to benzo(g,h,i)perylene.

2 - Ranking based on highest to lowest TPAH concentration.

3 - Ratio of Light PAH (LPAH = Σ Naphthalene to Phenanthrene) to Heavy PAH (HPAH = Σ Fluoranthene to Benzo(g,h,i)perylene) estimates the fraction of PAH that are potentially most subject to alteration by environmental weathering.

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Table 4
Diagnostic Source Ratios Calculated as Input for PCA

Sample ID	AY/ AE	DF/ F0	A0/ P0	FL0/ PY0	BB/ BAP	BJK/ BAP	BEP/ BAP	IND/ GHI	DBT2/ PA2	DBT3/ PA3	N0/ N2+N3	P0+A0/ PA2+PA3	DBT0/ DBT2+DBT3
2"Pipe	0.33	0.57	0.35	0.77	0.49	0.75	0.45	1.18	0.33	0.38	1.34	3.43	1.67
12"Pipe	0.32	0.58	0.32	0.76	0.51	0.72	0.45	1.19	0.30	0.36	1.37	3.37	1.69
TW-13	0.39	0.21	0.25	0.64	0.50	0.64	0.56	0.97	0.32	0.49	4.30	7.89	1.22
D East	0.28	0.24	0.33	0.66	0.37	0.44	0.40	0.98	0.36	0.59	1.31	7.41	0.96
S Gate 1	0.20	0.29	0.33	0.68	0.38	0.45	0.39	1.03	0.33	0.51	1.25	7.07	1.70
S Gate 2	0.17	0.27	0.33	0.67	0.38	0.43	0.39	1.00	0.32	0.49	1.94	7.55	1.15
D Center	0.21	0.26	0.22	0.47	0.51	0.60	0.55	0.94	0.31	0.52	1.49	5.91	0.87
S Center	0.23	0.27	0.30	0.72	0.56	0.66	0.59	0.98	0.30	0.47	1.38	6.13	0.82
UG Riser	0.19	0.20	0.30	0.65	0.45	0.50	0.49	1.00	0.35	0.53	1.34	6.44	0.91
East Riser	0.17	0.32	0.25	0.72	0.56	0.65	0.68	0.84	0.34	0.52	3.71	23.77	7.44
West Riser	0.23	0.20	0.31	0.67	0.45	0.47	0.46	0.95	0.33	0.53	0.69	6.20	0.98
Inside Discharge	0.11	0.19	0.28	0.65	0.52	0.65	0.57	0.98	0.35	0.54	1.47	7.55	1.07
Discharge	0.21	0.19	0.29	0.66	0.41	0.51	0.47	1.03	0.32	0.51	1.52	7.00	1.03
Solid Discharge	0.21	0.34	0.27	0.66	0.56	0.64	0.61	0.91	0.38	0.57	0.65	5.12	0.85
MW-7	0.17	0.28	0.33	0.65	0.52	0.62	0.60	0.90	0.43	0.61	0.14	2.77	0.53
TW-9	0.08	0.07	0.24	0.60	0.41	0.45	0.50	0.94	0.27	0.48	2.77	8.24	0.58
Solid Discharge (Dup)	0.21	0.33	0.28	0.66	0.53	0.66	0.61	0.92	0.38	0.57	0.65	5.54	0.87
Average	0.22	0.28	0.29	0.66	0.48	0.58	0.51	0.99	0.34	0.51	1.61	7.14	1.43
Std Dev	0.08	0.13	0.04	0.07	0.07	0.11	0.09	0.09	0.04	0.06	1.07	4.58	1.59
CV	0.36	0.45	0.13	0.10	0.14	0.18	0.17	0.09	0.11	0.13	0.67	0.64	1.11

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Attachment 3

Gas Chromatographic Fingerprints

Attachment 4

Quantitative GC/MS Data

Attachment 5

Guidance for Reviewing PAH Histograms

Attachment 6

PAH Histograms

Attachment 7

Biomarker Fingerprints:

Normal Alkanes and Alkylcyclohexanes

Appendix 8

Biomarker Fingerprints:

Terpanes

Appendix 9

Biomarker Fingerprints:

Steranes

Attachment 10

Chain of Custody